PATENT SPECIFICATION

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(54) IMPROVEMENTS IN FISCHER-TROPSCH SYNTHESIS

(71) We, SOUTH AFRICAN COAL, OIL AND GAS CORPORATION LIMITED, of Klasie Havenga Road, Sasolburg, O.F.S., Republic of South Africa, a South African Corporation, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a Fischer-Tropsch synthesis process for converting gases containing carbon monoxide and hydrogen (and carbon dioxide) in the presence of a Fischer-Tropsch catalyst into fluid products ranging from gaseous to liquids boiling up to and including the deisel oil range, preferably were carried out with a catalyst of the iron type.

The invention is particularly applicable to the synthesis of hydrocarbons, in particular aliphatic hydrocarbons of low to medium molecular weight, say ranging from methane up to hydrocarbons boiling in the diesel oil range. The reaction conditions can, however, be adjusted to produce greater or lesser relative yields of oxygenated compounds as well, in particular alcohols, fatty acids, esters, ketones and aldehydes, as is known to the person skilled in the art. Conventional Fischer-Tropsch processes are generally carried out at temperatures not exceeding about 250°C. Conventionally fixed bed Fischer-Tropsch reactors are usually operated at pressures up to about 27 kg/cm², whereas moving fluidized catalyst reactors are operated at pressures up to about 20 kg/cm². In order to increase the conversion rates it is desirable to carry out the synthesis at comparatively high temperatures, more particularly from 250°C upwards. At such higher temperatures however, in particular above 280°C, there is a tendency for the rate of carbon deposition on the catalyst to increase, and this can affect the economics and practicability of the process adversely. The exact limits within which the rate of carbon deposition is acceptable will vary from case to case, being very low in reactors which do not permit easy or inexpensive replacement or regeneration of the catalyst. A higher level is acceptable e.g. when using a circulating catalyst, particularly an inexpensive iron catalyst.

From the literature one would have expected that the rate of carbon deposition on Fischer-Tropsch catalysts, in particular on iron catalysts, is simply dependent on the ratio of hydrogen to carbon monoxide concentrations present or on the partial pressure of hydrogen alone. However, surprisingly that has now been found to be incorrect at higher temperatures.

It is an object of the invention to provide a process by means of which the rate of carbon laydown can be kept within acceptable limits at comparatively high temperatures, even though the ratio of hydrogen to carbon monoxide may be comparatively low.

In accordance with the present invention there is provided a process of the aforesaid type comprising the feature that it is carried out at temperatures from 280°C upwards and that the "carbon deposition factor", defined as

$$p_{co}/p^3_{H_2} \times 10^3$$

wherein p_{co} and

$$p_{H_2}$$

are the partial pressures of carbon monoxide and hydrogen measured in the feed gas entry region of the conversion space in units of kg/cm², is adjusted to a value of up to at the most 8 (kg/cm²)⁻² and that at the same time the basicity of the catalyst is set to a value equal to that of a pure iron catalyst to which has been added between zero and 0.001 g K_2O/m^2 (both values included) of effective catalyst surface, subject to the further limitation that where the carbon deposition factor equals or exceeds 4 (kg/cm²)⁻², the basicity as above defined is less than 0.0005 g K_2O/m^2.

Thus the rate of carbon build-up is proportional to

$p_{co}/p^3_{H_2}$.

These figures apply with a small margin of safety to the case where a rate of carbon build-up of up to 4 g carbon/100 g catalyst/day is acceptable. Surprisingly that rate of carbon build-up is tolerated readily by processes carried out with a circulating fluidised iron catalyst.

In order to have a greater margin of safety it is sometimes preferred to maintain a carbon deposition factor not exceeding $4(kg/cm^2)^{-2}$. In that case, applying the basicity criteria according to the previous paragraph, the rate of carbon build-up can be limited to about half the above value, i.e. 2 g carbon per 100 g catalyst per day.

Alternatively, by limiting the carbon deposition factor to 4, preferably 2, it becomes possible (without excessive carbon build-up rates) to use a catalyst of intermediate basicity, provided it is less than a basicity equal to an iron catalyst containing besides iron 0.0005 g K_2O/m^2 of effective catalyst surface area. Such higher basicities may be desirable if the product is to contain a comparitively high content of higher homologues of methane.

Thus a basicity equivalent to that of a pure iron catalyst promoted exclusively with between 0.0001 and 0.0005 g K_2O/m^2 of effective catalyst surface is usually preferred, a typical preferred upper limit being 0.0002 g K_2O/m^2.

An adequate margin of safety is usually attainable when the upper limits of basicity, taken as values equal to a given pure iron catalyst promoted exclusively with the stated amount of K_2O and the corresponding upper limits of the "carbon deposition factor" are selected in accordance with the following table

carbon dep. factor $\frac{P_{CO}}{p^3_{H_2}} \times 10^3\ (kg/cm^2)^{-2}$	gK_2O/m^2 of catalyst
2	0.0005
4	0.0002

and interpolated values as well as extrapolated values between the limits of 0.0001 and 0.001 g K_2O/m^2.

More accurately, when accepting 4 g carbon per 100 g catalyst per day as an acceptable rate of carbon build-up, the aforesaid upper limit of basicity and carbon deposition factor are interrelated by the formula:

$$C = 13 - a \times 10^4,$$

wherein C is the "carbon deposition factor

$$\frac{p_{co}}{p^3_{H_2}} \times 10^3\ (kg/cm^2)^{-2}$$

and a is the basicity expressed in terms of g/m^2 of K_2O evenly distributed in pure iron catalyst so as to attain that particular basicity, within the limits of 0.0001 and 0.001 g K_2O/m^2.

The above applies more particularly to temperatures between 300 and 340°C. The formula can be applied at higher temperatures if a correspondingly higher rate of carbon build-up is acceptable or if an appropriate correction factor (or margin of safety) is taken into account.

Within the above basicity limits the upper limit of the carbon deposition factor is directly proportion (for practical purposes) to the acceptable rate of carbon build-up. Accordingly there is also provided in accordance with the invention a method of controlling carbon deposition in Fischer-Tropsch synthesis between 300 and 340°C up to a predetermined "acceptable" upper limit of

b [g carbon/100 g catalyst/day],

wherein the upper limits of basicity, taken as values equal to a given pure iron catalyst promoted exclusively with the stated amount of K_2O and the corresponding upper limits of the "carbon deposition factor" are selected in accordance with the following formula

$$C = \frac{b}{4}[13 - a \times 10^4]$$

wherein C and a have the same meanings as above.

The numerical value of the carbon deposition factor will obviously vary depending on the units of pressure employed.

In the present process it is preferred to operate from pressures of 32 kg/cm^2 upwards, even in the case of a moving fluidised catalyst reactor, more particularly up to 70 kg/cm^2, say in the range of 35—70 kg/cm^2 thereby to lower the carbon deposition factor.

For a given partial pressure of carbon monoxide it is also possible in accordance with the present teachings to decrease the rate of carbon deposition by only increasing the partial pressure of hydrogen.

Surprisingly the partial pressure of carbon dioxide which has a decided influence on the composition of the synthesis products has virtually no influence on the rate of carbon formation.

As will be readily understood there will be practical limits to the minimum value of the parameter

$$(p_{co}/p^3_{H_2}) \times 10^3,$$

depending on the composition of the products aimed at. For example, for making a 1000 BTU gas at a pressure of 70 kg/cm^2 with a catalyst of zero alkalinity and at 320°C, the minimum value of that parameter is about 1(kg/cm^2)$^{-2}$ for an acceptable carbon build-up rate of 2 g/100 g catalyst/day, or 2(kg/cm^2)$^{-2}$ if double that build-up rate is accepted.

Although certain embodiments of the invention can be carried out even at higher temperatures, it is preferred to carry out the process between 280°C and 45/°C, more preferably between 300 and 400°C, more conveniently still between 300 and 360°C, the optimum temperature range from various practical points of view at present being considered to be between 305 and 330°C or at an average of about 320°C.

For the aforesaid definitions of basicity, a substantially pure iron catalyst, promoted only with the respective amounts of K_2O, fused and ground in the normal manner, was taken as standard for comparison. As will be readily understood by the person skilled in the art, the basicity of such catalysts can be varied in a variety of manners to achieve degrees of basicity which are empirically comparable with a given concentration of K_2O in pure iron catalyst (normally obtained from mill-scale). Thus for example, more Na_2O must be employed to achieve the same degree of basicity as a given amount of K_2O. Even high concentrations of lithium oxide achieve a comparatively low increase only in basicity for the purposes of the present invention. On the other hand, the effect of small additions of caesium oxide or rubidium oxide is comparatively greater than that of the same amount of K_2O. Acid components such as SiO_2 or TiO_2, result in a lowering of the basicity.

Structural promoters such as magnesium oxide, aluminium oxide, calcium oxide, titanium oxide, chromium oxide (Cr_2O_3),MnO etc. have the effect of increasing the effective surface area of the catalyst, and accordingly lowering the basicity per unit of effective surface area.

In addition the overall activity of the catalyst can be adjusted in manners known per se by the judicious addition of Group VIII (e.g. cobalt, nickel, platinum) and Group IB (e.g. copper) elements.

In principle the present invention is not limited to any particular type of synthesis reactor. However, because the process is carried out at comparatively high temperatures, it is preferred to carry out the process in those types of reactors which facilitate thermal control. More particularly, it is preferred to carry out the process with a catalyst maintained in an expanded condition by gas flowing therethrough either in a dilute phase expanded condition, i.e. a gas-entrained condition or in a dense phase fluidised condition, i.e. either a moving or stationary fluidised bed. If it is desired to operate under fixed catalyst bed conditions, it is preferred to employ what is known as a diluted fixed bed.

It will be readily understood by those skilled in the art that the performance of the present process does not depend entirely on the gas composition of the feed gas, but on the composition of the gas throughout its passage through the reactor. The partial pressure of carbon monoxide undergoes a very substantial change from the feed end to the outlet end of the reactor, whilst partial pressures of hydrogen and of carbon dioxide change less substantially. Also, in known types of reactors, the general patterns of these changes are substantially similar. Accordingly, it is possible from a practical point of view to define the parameters of the process in accordance with the invention with reference to the composition of the partial pressures of the components of the synthesis gas in the feed gas entry region of the reactor.

Example.

To illustrate the beneficial effect of higher pressures (i.e. lower

$$p_{co}/p^3_{H_2} \text{ values})$$

on the rate of carbon deposition the data in table 1 (which can be extrapolated for higher pressures) is presented. The catalyst used was one of intermediate basicity consisting of iron and some K_2O (corresponding to approximate 0.0005 g K_2O/m^2 of effective surface area). The catalyst had been prepared from mill-scale. All the data of table 1 were obtained at a temperature of 320°C, and the same feed gas composition and recycle ratio was used throughout.

TABLE 1

Total pressure kg/cm²	REACTOR			INLET		
	H₂/CO ratio	p_{H_2} kg/cm²	p_{CO} kg/cm²	p_{CO_2} kg/cm²	$p_{CO}/p^3_{H_2}$ × 10³	Carbon deposition rate *
9.6	4.6	3.94	0.91	1.12	15	17
13.1	4.3	5.27	1.19	1.55	7.5	9
18.4	4.6	7.45	1.62	1.90	3.9	4
21.9	5.0	9.85	1.97	2.11	2.1	2.6

* g carbon/100 g Fe per 100 h.

Note that in spite of the increasing CO partial pressure the rate of carbon laydown decreases which indicates that the p_{CO} alone certainly does not control carbon deposition. The increase in partial pressure of H_2 clearly more than compensates for the increase in CO pressure. Furthermore, it can be seen that the carbon deposition rate (which correlates with the carbon deposition factor) bears no relation with the H_2/CO ratio.

Even though it might appear from table 1 that the total reactor pressure also correlates with the rate of carbon deposition, this is not so in general. Thus all the data presented in tables 2 to 5 below are all at the same total pressure, yet the carbon deposition rates vary widely. The only consistent correlation is that with the carbon deposition factor as herein defined.

To further illustrate that the hydrogen pressure is important and not only the CO pressure in controlling carbon laydown the data in table 2 is presented.

TABLE 2

REACTOR INLET					
p_{H_2} kg/cm²	p_{CO} kg/cm²	p_{CO_2} kg/cm²	$\frac{H_2}{CO}$ ratio	$\frac{p_{CO}}{p^3_{H_2}}$ × 10³	Carbon deposition rate
6.12	1.83	1.27	3.3	8.3	7.5
7.25	1.76	0.91	4.1	4.6	5.6
10.1	1.69	0.71	6.0	1.6	2.0

In these runs the CO partial pressures were very similar while the H_2 pressures were varied. With increasing hydrogen pressure the carbon deposition clearly decreased.

That the CO_2 pressure does not influence the rate of carbon formation is illustrated in the data in table 3 where the CO and H_2 pressures were kept virtually constant while the CO_2 pressure was varied.

TABLE 3

p_{H_2} kg/cm²	p_{CO} kg/cm²	p_{CO_2} kg/cm²	$\frac{H_2}{CO}$	$\frac{p_{CO}}{p^3_{H_2}} \times 10^3$	Carbon deposition rate
7.25	1.67	0.91	4.1	4.6	5.6
7.45	1.62	1.90	4.6	3.9	4.2
7.53	1.62	2.46	4.6	3.8	4.2
7.66	1.76	4.36	4.4	3.9	5.1

Table 4 will show that there is no real relation between the H_2/CO ratio and carbon deposition rate.

TABLE 4

H_2/CO	pH_2 kg/cm²	p_{CO} kg/cm²	p_{CO_2} kg/cm²	$\frac{p_{CO}}{p^3_{H_2}} \times 10^3$	Carbon deposition rate
4.6	7.46	1.62	1.90	3.9	4.2
4.2	7.10	1.69	2.81	4.7	4.2
4.6	5.56	1.27	1.41	6.7	10
4.3	3.94	0.91	1.13	15	17

The data in table 5 are for a series of runs (zero alk.cat.) in which the hydrogen partial pressures were approximately constant with varying CO pressures.

TABLE 5

p_{H_2} kg/cm²	p_{CO} kg/cm²	$\frac{p_{CO}}{p^3_{H_2}} \times 10^3$	Carbon deposition rate
10.6	2.60	2.2	11
11.0	1.76	1.3	5
10.3	0.63	0.6	3

The results show that the carbon deposition increases with the CO pressure. Overall, hence, the carbon deposition depends on both the CO and the H_2 partial pressures but not on the simple ratio H_2/CO. The parameter

$$p_{CO}/p_{H_2}^3,$$

which because of the cubic power factor stresses the importance of the actual pressures involved, satisfactorily reflects the situation.

From the mathematical nature of the carbon deposition factor (the power factor "3" in the hydrogen partial pressure being, of course an approximation), it follows that one of the simplest ways to decrease the rate of carbon deposition is to increase the total pressure. Thus a feed gas with a low H_2/CO ratio which at low pressures results in high carbon deposition rates, could be successfully utilised by increasing the total pressure. This makes possible the utilisation of lower H_2/CO ratio gases which are cheaper to manufacture than high H_2/CO ratio gases.

WHAT WE CLAIM IS:—

1. Fischer-Tropsch synthesis process for converting gases comprising carbon monoxide and hydrogen (and carbon dioxide) in the presence of a Fischer-Tropsch catalyst into fluid products ranging from gaseous to liquids boiling up to and including the diesel oil range comprising the feature that it is carried out at temperatures from 280°C upwards and that the "carbon deposition factor", defined as

$$p_{CO}/p^3_{H_2} \times 10^3$$

wherein p_{CO} and p_{H_2} are the partial pressures of carbon monoxide and hydrogen measured in the feed gas entry region of the conversion space in units of kg/cm^2, is adjusted to a value of up to at the most 8 $(kg/cm^2)^{-2}$ and that at the same time the basicity of the catalyst is set to a value equal to that of a pure iron catalyst to which has been added between zero and 0.001 g K_2O/m^2 (both values included) of effective catalyst surface, subject to the further limitation that where the carbon deposition factor equals or exceeds 4 $(kg/cm^2)^{-2}$, the basicity as above defined is less than 0.0005 g K_2O/m^2.

2. Process according to claim 1, wherein the upper limit of the carbon deposition factor is 4 $(kg/cm^2)^{-2}$.

3. Process according to claim 1 or 2 carried out with a catalyst having a basicity equal to that of a pure iron catalyst promoted exclusively with between 0.0001 and 0.0005 g K_2O/m^2 of effective catalyst surface.

4. Process according to any one of claims 1 to 3 carried out with a catalyst having a basicity equal to that of a pure iron catalyst promoted exclusively with up to 0.0002 g K_2O/m^2 of effective catalyst surface and wherein the upper limit of the carbon deposition factor is 4 $(kg/cm^2)^{-2}$.

5. Process according to claim 1 wherein the upper limits of basicity, taken as values equal to a given pure iron catalyst promoted exclusively with the stated amount of K_2O and the corresponding upper limits of the "carbon deposition factor" are selected in accordance with the following table

carbon dep. factor $\frac{p_{CO}}{p^3_{H_2}} \times 10^3$ $(kg/cm^2)^{-2}$	g K_2O/m^2 of catalyst
2	0.0005
4	0.0002

and interpolated values as well as extrapolated values between the limits of 0.0001 and 0.001 g K_2O/m^2.

6. Process according to any one of claims 1 to 5 carried out at a reactor pressure from 32 kg/cm^2 upwards.

7. Process according to claim 6, carried out at a reactor pressure between 35 and 70 kg/cm^2.

8. Process according to any one of claims 1 to 7 carried out at between 280°C and 450°C.

9. Process according to claim 8 carried out at between 300 and 400°C.

10. Process according to claim 9 carried out at between 300 and 360°C.

11. Process according to claim 10 carried out at between 305 and 330°C.

12. Process according to any one of claims 1 to 11, carried out with the catalyst maintained in an expanded condition by gas flowing therethrough.

13. Process according to claim 12 carried out with the catalyst in a gas-entrained condition.

14. Process according to claim 12 carried out with the catalyst in a moving fluidized bed.

15. Process according to claim 12 carried out with the catalyst in a stationary fluidised bed.

16. Process according to any one of claims 1 to 15, applied to the manufacture of high thermal value gas.

17. Process according to any one of claims 1 to 16 wherein the upper limits of basicity, taken as values equal to a given pure iron catalyst promoted exclusively with the stated amount of K_2O and the corresponding upper limits of the "carbon deposition factor" are selected in accordance with the following formula:

$$C = 13 - a \times 10^4,$$

wherein C is the carbon deposition factor

$$\frac{p_{co}}{p^3_{H_2}} \times 10^5 \ (kg/cm^2)^{-2}$$

and a is the basicity expressed in terms of g/m^2 of K_2O evenly distributed in pure iron catalyst so as to attain that particular basicity within the limits of 0.0001 and 0.001 g K_2O/m^2.

18. A method of controlling carbon deposition in Fischer-Tropsch synthesis between 300 and 340°C up to a predetermined "acceptable" upper limit of

$$b[\text{g carbon/100 g catalyst/day}],$$

wherein the upper limits of basicity, taken as values equal to a given pure iron catalyst promoted exclusively with the stated amount of K_2O and the corresponding upper limits of the "carbon deposition factor" are selected in accordance with the following formula:

$$C = \frac{b}{4}(13 - a \times 10^4),$$

wherein C is the "carbon deposition factor

$$\frac{p_{co}}{p^3_{H_2}} \times 10^3 [(kg/cm^2)^{-2}]$$

and a is the basicity expressed in terms of g/m^2 of K_2O evenly distributed in pure iron catalyst so as to attain that particular basicity, with the limits of 0.001 and 0.001 g K_2O/m^2

19. Process according to claim 1 substantially as hereinbefore described.

20. A method of controlling carbon deposition in Fischer-Tropsch synthesis substantially as hereinbefore described by way of example.

21. Synthesis products whenever produced by a process or with a method as claimed in any one of claims 1 to 20.

22. High thermal value gas whenever produced by a process or with a method as claimed in any one of claims 1 to 20.

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